

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 757 088 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
07.06.2000 Bulletin 2000/23

(51) Int Cl.7: **C09K 11/06, H05B 33/14**

(21) Application number: **96305743.5**

(22) Date of filing: **05.08.1996**

(54) **Organoelectroluminescence device material and organoelectroluminescence device for which the material is adapted**

Organisches elektrolumineszentes Element und leuchtemittierende Vorrichtung mit diesem Element

Élément électroluminescent organique et dispositif émettant de la lumière utilisant cet élément

(84) Designated Contracting States:
DE FR GB

(30) Priority: **04.08.1995 JP 19933995**

(43) Date of publication of application:
05.02.1997 Bulletin 1997/06

(73) Proprietor: **TOYO INK MANUFACTURING CO., LTD.**
Tokyo (JP)

(72) Inventors:
• **Enokida, Toshio, Toyo Ink Manufac. Co., Ltd.**
Tokyo (JP)
• **Tamano, Michiko, Toyo Ink Manufac. Co., Ltd.**
Tokyo (JP)
• **Okutsu, Satoshi, Toyo Ink Manufac. Co., Ltd.**
Tokyo (JP)

(74) Representative: **Woods, Geoffrey Corlett**
J.A. KEMP & CO.
Gray's Inn
14 South Square
London WC1R 5LX (GB)

(56) References cited:
EP-A- 0 554 569

- **POLYM. MATER. SCI. ENG. (1995), 72, 331-2**
CODEN: PMSDGG;ISSN: 0743-0515, 1995,
XP000671148 SAPOCHAK, LINDA S. ET AL:
"Luminescent properties of pentacoordinated
gallium bis(2-methyl-8-hydroxyquinoline)
(carboxylate and chloro) compounds for OLED
applications"
- **APPLIED PHYSICS LETTERS, 16 MAY 1994,**
USA, vol. 64, no. 20, ISSN 0003-6951, pages
2718-2720, XP000449711 BURROWS P E ET AL:
"Metal ion dependent luminescence effects in
metal tris-quinolate organic heterojunction light
emitting devices"

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 757 088 B1

Description

[0001] The present invention relates to an organoelectroluminescence ("EL" hereinafter) device used as a flat light source or display, more specifically to a light-emitting device having a high brightness.

[0002] An EL device using an organic substance is greatly expected to be usable as a solid light-emitting inexpensive large-screen, full-color display device, and the development thereof is being made in many ways. Generally, an EL device is composed of a light-emitting layer and a pair of mutually opposite electrodes sandwiching the light-emitting layer. Light emission is the following phenomenon. When an electric field is applied between these two electrodes, the cathode injects electrons into the light-emitting layer, and the anode injects holes into the light-emitting layer. When the electrons recombine with the holes in the light-emitting layer, their energy level shifts to a valence bond band to release energy as fluorescent light.

[0003] As compared with inorganic EL devices, conventional organic EL devices require high voltage, and their light emission brightness and light emission efficiency are low. Further, conventional organic EL devices deteriorate in properties to a great extent, and no organic EL device has been put to practical use.

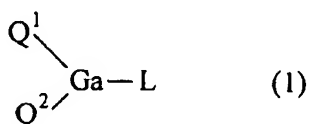
[0004] There has been recently proposed an organic EL device which is produced by laminating a thin film containing an organic compound having a fluorescent quantum effect of emitting light at a low voltage as low as less than 10 V, and it attracts attention (Appl. Phys. Lett., Vol. 51, page 913, 1987). The above organic EL device has a fluorescent layer containing a metal chelate complex and a hole-injecting layer containing an amine-based compound, and emits green light having a high brightness. The above organic EL device achieves nearly practically usable performance, since it accomplishes a brightness of 1,000 cd/m² and a maximum light emission efficiency of 1.5 lm/W at a direct current voltage of 6 or 7V.

[0005] However, conventional organic EL devices including the above organic EL device are not yet satisfactory in brightness although these organic EL devices are improved in brightness to some extent. The serious problem is that they are insufficient in light emission stability in their continuous operation for a long period of time. Fewer materials which emit blue light perform adequate brightness or light emission efficiency, and it has been desired to develop light-emitting materials for the device.

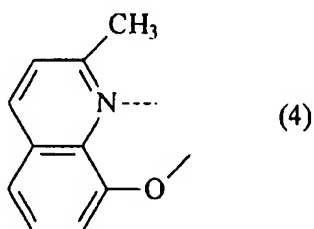
[0006] It is an object of the present invention to provide a material which can give an organic EL device excellent in stability in the repetitive operation, and an organic EL device for which the material is adapted.

[0007] It is another object of the present invention to provide a material which can give an organic EL device which has a high light emission brightness and is excellent in stability in the repetitive operation, and an organic EL device for which the material is adapted.

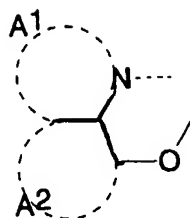
[0008] Accordingly, the present invention provides the use of a compound of formula (1) in an electron injecting layer of an organic electroluminescence device,



wherein at least one of Q¹ and Q² is a ligand of formula (4),



the other being a ligand of the general formula (2),



(2)

wherein A¹ and A² are substituted or unsubstituted six-membered aryl rings which are mutually fused to form a fused ring moiety, and

L is -OR¹ in which R¹ is a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group or a substituted or unsubstituted aryl group.

[0009] According to the present invention, there is also provided an organic electroluminescence device comprising a plurality of thin organic compound layers including a light-emitting layer and an electron-injecting layer, sandwiched between an anode and a cathode, wherein the electron-injecting layer comprises a compound of formula (1).

[0010] Fig. 2 is shows an infrared absorption spectrum of Compound (2).

[0011] Fig. 3 is shows an infrared absorption spectrum of Compound (9).

[0012] Fig. 4 is shows an infrared absorption spectrum of Compound (12).

[0013] Fig. 5 is shows an infrared absorption spectrum of Compound (16).

[0014] Fig. 6 is shows an infrared absorption spectrum of Compound (17).

[0015] In the general formula (1), the ligands represented by Q¹ and Q² include quinoline moieties such as 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline, while the ligand shall not be limited to these.

[0016] In the general formula (2), A¹ and A² are substituted or unsubstituted six-membered aryl rings which are mutually fused to form a fused ring moiety. The fused ring moiety has the structure of an aryl ring or a heterocyclic ring. The metal complex in the present invention has a stronger quality as an n-type semiconductor anti the high capability of injecting electrons. Further, since the formation energy at a complex formation time is low, the bonding strength of the metal and the ligands in the metal complex is high, and the fluorescence quantum efficiency as a light-emitting material is high.

[0017] Specific examples of the substituent on the fused ring of A¹ and A² forming the ligand of the general formula (2) include halogen atoms such as chlorine, bromine, iodine and fluorine; substituted or unsubstituted alkyl groups such as methyl, ethyl, propyl, butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, stearyl and trichloromethyl; substituted or unsubstituted aryl groups such as phenyl, naphthyl, 3-methylphenyl, 3-methoxyphenyl, 3-fluorophenyl, 3-trichloromethylphenyl, 3-trifluoromethylphenyl and 3-nitrophenyl; substituted or unsubstituted alkoxy groups such as methoxy, n-butoxy, tert-butoxy, trichloromethoxy, trifluoroethoxy, pentafluoropropoxy, 2,2,3,3-tetrafluoropropoxy, 1,1,1,3,3,3-hexafluoro-2-propoxy and 6-(perfluoroethyl)hexyloxy; substituted or unsubstituted aryloxy groups such as phenoxy, p-nitrophenoxy, p-tert-butylphenoxy, 3-fluorophenoxy, pentafluorophenoxy and 3-trifluoromethylphenoxy; substituted or unsubstituted alkylthio groups such as methylthio, ethylthio, tert-butylthio, hexylthio, octylthio and trifluoromethylthio; substituted or unsubstituted arylthio groups such as phenylthio, p-nitrophenylthio, p-tert-butylphenylthio, 3-fluorophenylthio, pentafluorophenylthio and 3-trifluoromethylphenylthio; mono- or di-substituted amino groups such as cyano, nitro, amino, methylamino, dimethylamino, ethylamino, diethylamino, dipropylamino, dibutylamino and diphenylamino; acylamino groups such as bis(acetoxymethyl)amino, bis(acetoxyethyl)amino, bis(acetoxypropyl)amino and bis(acetoxybutyl)amino; carbamoyl groups such as hydroxyl, siloxy, acyl, methylcarbamoyl, dimethylcarbamoyl, ethylcarbamoyl, diethylcarbamoyl, propylcarbamoyl, butylcarbamoyl and phenylcarbamoyl; carboxyl acid group; sulfonic acid group; imido group; cycloalkyl groups such as cyclopentyl and cyclohexyl; aryl groups such as phenyl, naphthyl, biphenyl, anthranyl, phenanthryl, fluorenyl and pyrenyl; and heterocyclic groups such as pyrazinyl, pyrazinyl, pyrimidinyl, pyridazinyl, triazinyl, indolyl, quinolyl, acridinyl, pyrolidinyl, dioxanyl, piperidinyl, morpholinyl, piperazinyl, triazinyl, carbazoyl, furanyl, thiophenyl, oxazolyl, oxadiazolyl, penzoxazolyl, thiazolyl, thiadiazolyl, benzothiazolyl, triazolyl, imidazolyl, benzoimidazolyl and puranyl. Further, any two members of the above substituents may bond together to form a six-membered aryl ring or heterocyclic ring.

[0018] The gallium complex of the present invention can give an organic EL device having high performances. When the gallium complex of the present invention is used in an electron-injecting layer which is in contact directly to a cathode, the device has the high capability of transporting electrons and the high capability of accepting electrons from a cathode, and the gallium complex of the present invention is therefore a remarkably advantageous material for an organic EL device. Further, most of the gallium complexes of the present invention have a melting point of at least 300°C, and this point is advantageous for manufacturing an organic EL device having a high light emission brightness and a long life.

[0019] Specific examples of the ligand L or the substituents include those described concerning the rings A¹ and A².

[0020] Typically, Q¹ and Q² are both ligands of the formula (4).

[0021] The gallium complex of the general formula (1), provided by the present invention, can be synthesized, for example, from gallium as a metal or a gallium compound and compound(s) having ligand residues of Q¹ and Q² or L. The gallium compound includes alkyl gallium, gallium halide, gallium acetate, gallium nitrate, gallium arsenide, gallium nitride, gallium phosphide, gallium sulfide, gallium selenide, gallium telluride, gallium hydroxide, gallium oxide, gallium alkoxides such as trimethoxygallium, triethoxygallium and triisopropoxygallium, and diethylgallium chloride. Part of each of these gallium compounds may be replaced with acetylacetonate. In view of reactivity and safety in the synthesis, gallium alkoxides are preferred although the gallium compound shall not be limited thereto.

[0022] The solvent used in the synthesis is selected from methanol, ethanol, isopropanol, ethyl acetate, acetonitrile, 1,4-dioxane, tetrahydrofuran, benzene, toluene, xylene, n-hexane, dimethylformamide, quinoline, sulfolane or water. The reaction temperature is determined depending upon the rate of the ligand forming the gallium complex. The temperature for the synthesis is preferably between 0°C and 250°C, more preferably 20°C and 80°C. The synthesis is carried out for 10 minutes to 24 hours. However, the synthesis conditions shall not be limited to the above-specified, since the synthesis conditions are determined depending upon the gallium compound, the ligand, the solvent and a catalyst used for the synthesis.

[0023] The gallium complex of the general formula (1) can be obtained by reacting gallium or the above gallium compound with a ligand residue (ligand compound) having a great steric hindrance as a compound for forming ligand residues represented by Q¹ and Q², to bond two ligand residues per gallium atom. The ligand L optionally bonds to a residue and constitutes the gallium complex of the present invention. Gallium strongly bonds to an alkyl group, an oxygen atom and a halogen atom and can form a stable gallium complex. Further, it is difficult to form a stable aluminum complex with 8-hydroxyquinoline having an alkyl group on the 2-position such as 2-methyl-8-hydroxyquinoline, while gallium can form a stable gallium complex with such a 8-hydroxyquinoline having an alkyl group on the 2-position. Gallium is therefore advantageous in this point.

[0024] Table 1 specifically shows typical examples (Compounds (1) to (28)) of the compound of the general formula (1), although the compound of the general formula (1) shall not be limited to these.

Table 1 (continued)

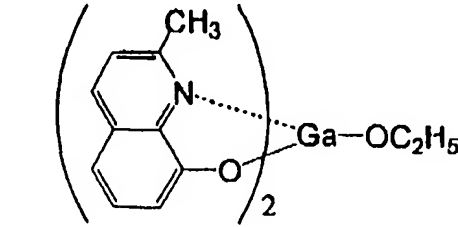
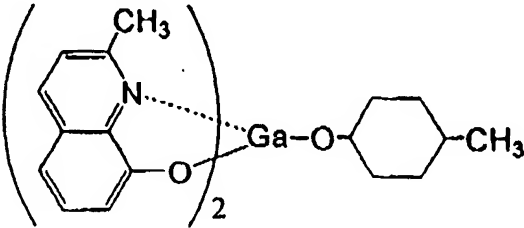
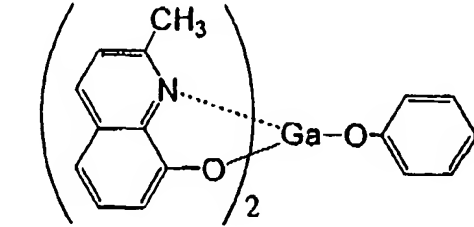
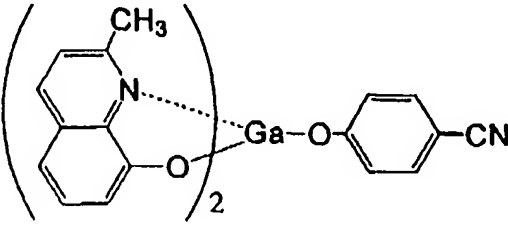
Compound	Chemical structure
(5)	
(6)	
(7)	
(8)	

Table 1 (continued)

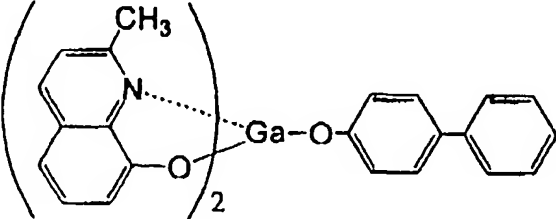
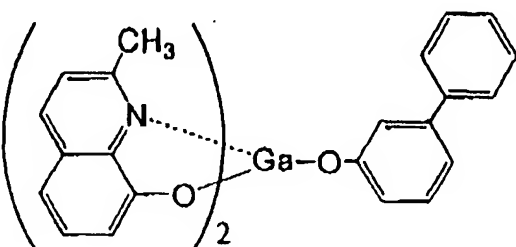
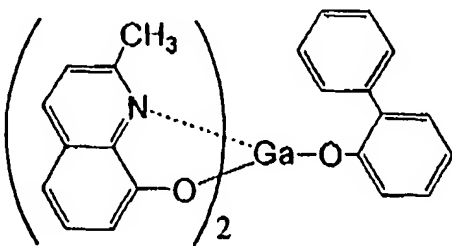
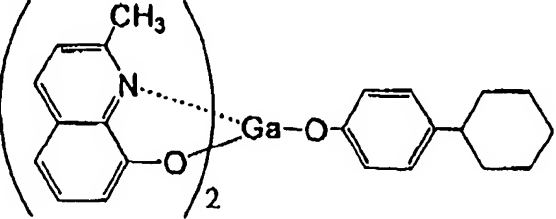
Compound	Chemical structure
(9)	
(10)	
(11)	
(12)	

Table 1 (continued)

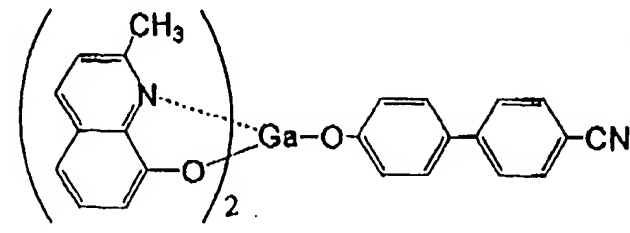
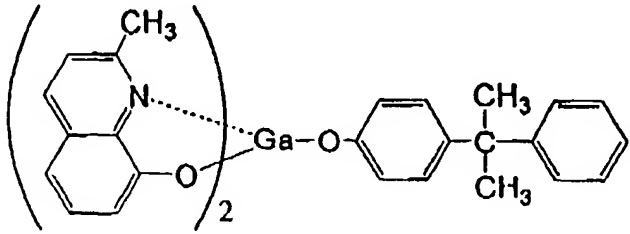
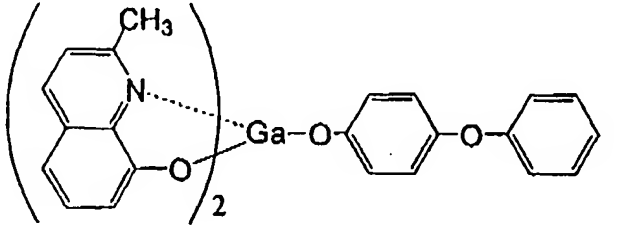
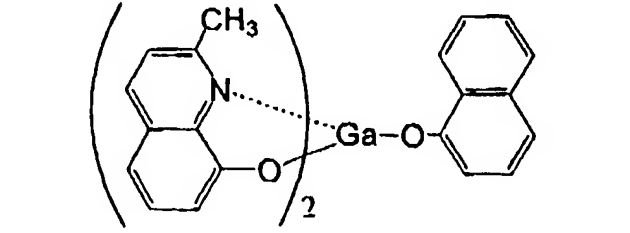
Compound	Chemical structure
(13)	
(14)	
(15)	
(16)	

Table 1 (continued)

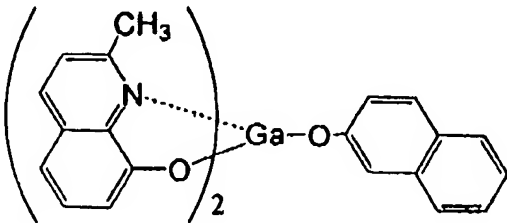
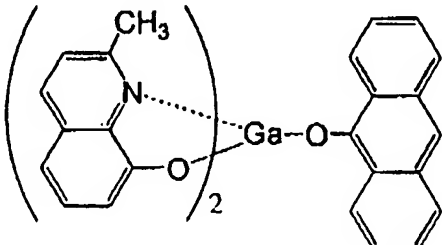
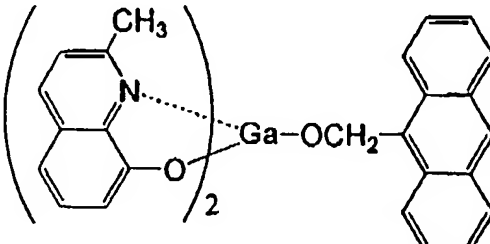
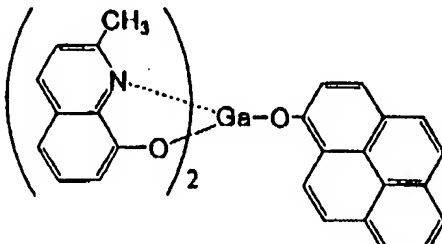
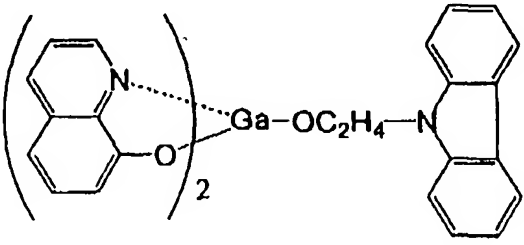
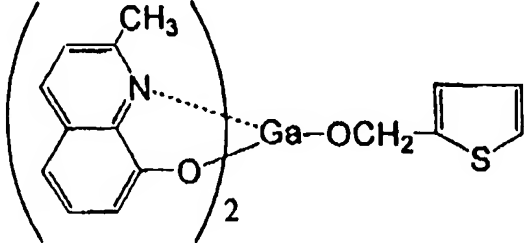
Compound	Chemical structure
(17)	
(18)	
(19)	
(20)	

Table 1 (continued)

Compound	Chemical structure
(2 2)	
(2 4)	

[0025] The above gallium complex can be adjusted to one having a necessary purity by cleaning it with water and/or an organic solvent, recrystallization from a proper solvent, a sublimation purification method or a combination of these.

[0026] The organic EL device of the invention can be manufactured by forming a plurality of thin organic compound layers between an anode and a cathode. The organic EL device of the present invention has a layer structure such as anode/light-emitting layer/electron-injecting layer/cathode, or anode/hole-injecting layer/light-emitting layer/electron-injecting layer/cathode. The compound of the general formula (1) can transport holes or electrons. However, it is used in the electron-injecting layer in the present invention since it is superior in the capability of transporting electrons. Further, the compound of the general formula (1) can be used as a light-emitting layer as well as in the electron injecting layer, since EL devices having light-emitting layers containing compounds of the general formula (1) emit fluorescence of intense blue to intense green. Therefore, the compound of the general formula (1) can give an organic EL device having high light emission characteristics.

[0027] A multi-layer structure of the organic EL device can serve to prevent quenching from degrading the brightness and the device life. Further, at least two members of a light-emitting material, a dopant, and a hole-injecting material and an electron-injecting material for carrier transportation may be used in combination. Further, each of the hole-injecting layer, the light-emitting layer and the electron-injecting layer may have the structure of at least two layers, and a device structure is selected such that holes or electrons can be effectively injected from the anode or the cathode and effectively transported through a layer.

[0028] When the gallium complex of the present invention is used as an electron-injecting material, the light-emitting material or the dopant which can be used together is selected from known materials such as naphthalene, anthracene, phenanthrene, pyrene, tetracene, coronene, chrysene, fluorescein, perylene, phthaloperylene, naphthaloperylene, perinone, naphthaloperinone, diphenylbutadiene, tetraphenylbutadiene, coumarine, oxadiazole, aldazine, bisbenzoxazoline, bisstyryl, diamine, pyrazine, cyclopentadiene, quinoline metal complex, aminoquinoline metal complex, benzoquinoline metal complex, imine, diphenylethylene, vinyl anthracene, diaminocarbazole, pyrane, thiopyrane, polymethine, merocyanine, an imidazole-chelated oxynoid compound, quinacridone, rubrene and derivatives of these, although the above materials shall not be limited to these. In particular, a metal complex compound, a bisstyryl compound, a conjugated polymer and an arylamine derivative are suitable as a light-emitting material. Typically, in the electroluminescence device of the invention, at least one of the layers comprises an arylamine derivative.

[0029] The above metal complex compound includes lithium (8-hydroxyquinolate), zinc bis(8-hydroxyquinolate),

manganese bis(8-hydroxyquinolate), copper bis(8-hydroxyquinolate), aluminum tris(8-hydroxyquinolate), gallium tris(8-hydroxyquinolate), beryllium bis(10-hydroxybenzo[h]quinolate), zinc bis(10-hydroxybenzo[h]quinolate), magnesium bis(10-hydroxybenzo[h]quinolate), aluminum tris(10-hydroxybenzo[h]quinolate), chlorogallium bis(2-methyl-8-quinolate), gallium bis(2-methyl-8-quinolate)(o-cresolate), aluminum bis(2-methyl-8-quinolate)(1-phenolate), gallium bis(2-methyl-8-quinolate)(2-phenolate), aluminum bis(2-methyl-8-quinolate)(1-naphtholate), gallium bis(2-methyl-8-quinolate)(1-naphtholate), zinc bis(2-[2-benzoxazolate]phenolate), and zinc bis(2-[2-benzothiazolate]phenolate). The above compounds may be used alone or in combination.

[0030] The above bisstyryl compound includes divalent residues which may have a substrate as a binding group such as phenylene residue, naphthylene residue, biphenylene residue, anthranylene residue, pyrenylene residue, thiophenylene residue, triphenylamine residue and N-ethylcarbazole residue. Specific examples of the bisstyryl compound include diphenylamino-1,4-bisstyrylbenzene, ditrylamino-1,4-bisstyrylbenzene, diphenylamino-4,4'-bisstyrylbiphenyl, 3-(N-ethylcarbazole)-4,4'-bisstyrylbiphenyl, and bis(4,4'-[2,2-diphenylvinyl])biphenyl. The above compounds may be used alone or in combination.

[0031] The conjugated polymer is typically a polymer having 2 to 10,000 recurring units, obtained by polymerizing only an arylene which may contain a nitrogen, oxygen or sulfur atom, or by polymerizing the arylene and a conjugated compound such as a vinyl compound. Specific examples of the conjugated polymer include poly(p-phenylene), poly(o-thiophene), poly(p-phenylenevinylene), poly(2,5-dipentyl-p-phenylenevinylene), poly(2,5-dipentyl-m-phenylenevinylene), poly(2,5-diethyl-p-phenylenevinylene), poly(2,5-dihexyloxy-p-phenylenevinylene), poly(2,5-dihexyloxy-m-phenylenevinylene), poly(2,5-dihexylthio-p-phenylenevinylene), poly(2,5-didecyloxy-p-phenylenevinylene), poly(2-methoxy-5-hexyloxy-p-phenylenevinylene), poly(2,5-thienylenevinylene), poly(3-n-octyl-2,5-thienylenevinylene), poly(1,4-naphthalenevinylene), poly(9,10-anthracenevinylene) and a copolymer obtained from at least two members of these. The above compounds may be used alone or in combination.

[0032] The above arylamine derivative is typically a compound obtainable by substituting a substituted diamino group in an arylene which may contain a nitrogen, oxygen or sulfur atom. Specific examples of the arylamine derivative include N,N,N',N'-(4-methylphenyl)-1,4'-phenyl-4,4'-diamine, N,N,N',N'-(4-methylphenyl)-1,3'-phenyl-4,4'-diamine, N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-(4-methylphenyl)-N,N'-(4-n-butylphenyl)-phenanthrene-9,10-diamine, N,N'-diphenyl-N,N'-dinaphthyl-1,1'-biphenyl-4,4'-diamine, N,N,N',N'-(4-methylphenyl)-1,4-naphthyl-4,4'-diamine, N,N,N',N'-(4-n-octylphenyl)-9,10-anthracene-4,4'-diamine, and N,N,N',N'-(4-(α,α' -dimethylbenzyl)phenyl)-anthracene-9,10-diamine. The above compounds may be used alone or in combination.

[0033] The hole-injecting material is a material which is capable of transporting holes, receiving holes from an anode, injecting holes into a light-emitting layer or light-emitting material, preventing excitons generated in a light-emitting layer from moving an electron-injecting layer or electron-injecting material and forming a thin film. Although not specially limited, specific examples of the hole-injecting material include a phthalocyanine derivative, a naphthalocyanine derivative, a porphyrin derivative, oxadiazole, triazole, imidazole, imidazolone, imidazolthione, pyrazoline, pyrazolone, tetrahydroimidazole, hydrazone, acylhydrazone, polyarylethane, stilbene, butadiene, benzidine type triphenylamine, styrylamine type triphenylamine, diamine type triphenylamine, derivatives of these, and polymer materials such as polyvinylcarbazole, polysilane and an electrically conductive polymer.

[0034] Further electron-injecting materials suitable for use in the electroluminescence device of the invention include materials capable of transporting electrons, receiving electrons from a cathode, injecting electrons into a light-emitting layer or light-emitting material, preventing excitons generated in the light-emitting layer from moving into a hole-injecting layer or hole-injecting material and forming a thin film. Although not specially limited, examples of the electron-injecting material include fluorenone, anthraquinodimethane, diphenylquinone, thiopyran dioxide, oxadiazole, thiadiazole, triazole, tetrazole, imidazole, perylene-tetracarboxylic acid, fluorenylidene methane, anthraquinodimethane, anthrone, a metal complex and derivatives of these. The hole-injecting material may be sensitivity-increased by incorporating an electron-accepting material, and the electron-injecting material may be sensitivity-increased by incorporating an electron-donating material. Further, the hole-injecting material can be selected from the above hole-injecting materials.

[0035] The light-emitting layer of the electroluminescence device of the invention may contain a compound of formula (1). It may also contain at least one selected from a light-emitting material, a dopant, a hole-injecting material or an electron-injecting material in combination with the gallium complex of the present invention. Further, the gallium complex of the present invention can be used in/as an electron-injecting layer between a light-emitting layer and a cathode since it is highly capable of receiving electrons from a cathode of a metal and transporting the electrons.

[0036] The electrically conductive material used for the anode of the organic EL device is suitably selected from those materials having a work function of greater than 4 eV. This electrically conductive material includes carbon, aluminum, vanadium, iron, cobalt, nickel, tungsten, silver, gold, platinum, palladium, alloys of these, metal oxides such as tin oxide and indium oxide used for ITO substrates or NESA substrates, and organic electrically conductive resins such as polythiophene and polypyrrole.

[0037] The electrically conductive material used for the cathode is suitably selected from those having a work function of smaller than 4 eV. This electrically conductive material includes magnesium, calcium, tin, lead, titanium, yttrium,

lithium, ruthenium, manganese, aluminum and alloys of these, while it shall not be limited to these. Typical examples of the alloys include magnesium/silver, magnesium/indium and lithium/aluminum, while the alloys shall not be limited to these. The metal ratio of the alloy is properly controlled by controlling the temperature of a deposition source, atmosphere and the degree of vacuum. Each of the anode and the cathode may have a structure of at least two layers as required.

[0038] For the effective light emission of the organic EL device, at least one of the electrodes is desirably transparent in the light emission wavelength region of the device. Further, the substrate is desirably transparent. The transparent electrode is produced from the above electrically conductive material by a deposition method or a sputtering method such that a predetermined transparency is secured. The electrode which forms a light emission surface preferably has a light transmittance of at least 10 %. The substrate is not specially limited if it has adequate mechanical and thermal strength and is transparent. For example, it is selected from glass substrates and substrates of transparent resins such as a polyethylene substrate, a polyethylene terephthalate substrate, a polyether sulfone substrate and a polypropylene substrate.

[0039] Each of the layers forming the organic EL device of the present invention can be formed by any one of dry film forming methods such as a vacuum deposition method, a sputtering method, a plasma method and an ion plating method and wet film forming methods such as a spin coating method, a dipping method and a flow coating method. The thickness of each layer is not specially limited, while each layer is required to have a proper thickness. When the layer thickness is too large, inefficiently, a high voltage is required to achieve predetermined emission of light. When the layer thickness is too small, the layer is liable to have a pinhole, etc., so that sufficient light emission brightness is hard to obtain when an electric field is applied. Generally, the thickness of each layer is preferably in the range of from 5 nm to 10 μ m, more preferably 10 nm to 0.2 μ m.

[0040] In the wet film forming method, a material for forming an intended layer is dissolved or dispersed in a proper solvent, and a thin film is formed from the solution or dispersion. The solvent is selected from ethanol, chloroform, tetrahydrofuran and dioxane, while the solvent shall not be limited to these. For improving the film formability and preventing the occurrence of pinholes, the above solution or dispersion for forming the layer may contain a proper resin and a proper additive. The resin suitable for use in the present invention includes insulating resins such as polystyrene, polycarbonate, polyarylate, polyester, polyamide, polyurethane, polysulfone, polymethyl methacrylate, polymethyl acrylate and cellulose, copolymers of these, photoconductive resins such as poly-N-vinylcarbazole and polysilane, and electrically conductive resins such as polythiophene and polypyrrole. The above additive includes an antioxidant, an ultraviolet absorbent and a plasticizer.

[0041] For improving the organic EL device of the present invention in the stability against temperature, humidity and ambient atmosphere, a protective layer may be formed on the surface of the device, or the device as a whole may be sealed with a silicone oil, or the like.

[0042] In the present invention, the organic EL device has an electron-injecting layer which contains the gallium complex of the general formula (1), and is therefore improved in properties such as light emission efficiency, maximum light emission brightness, etc. Further, the organic EL device is highly stable against heat and electric current, and further it exhibits practically usable light emission brightness at a low voltage, so that the deterioration of the device, a vital problem of prior art devices, can be remarkably decreased.

[0043] The organic EL device of the present invention can be applied to a flat panel display of a wall-mountable TV set, a light source for a copying machine or a printer, a light source for a liquid crystal display or a counter, a display board and a sign lamp as a flat light-emitter. The organic EL device of the present invention is therefore greatly industrially valuable.

Examples

[0044] The present invention will be further explained with reference to Examples hereinafter. Examples used glass substrates with ITO electrode having a surface resistance of 10 (Ω/\square) for producing organic EL devices.

Synthesis Example 1

[0045] 5.0 Grams of trimethoxygallium and 100 g of anhydrous ethanol were placed in a flask and stirred. Further, a solution of 9.0 g of 8-hydroxyquinoline in 140 g of anhydrous ethanol was dropwise added, and the mixture was stirred at 60°C for 30 minutes. Further, 2.9 g of phenol was added, and the mixture was stirred at 70°C for 30 minutes. Then, 4.9 g of 8-hydroxyquinoline was added, and the mixture was stirred at 70°C for 5 hours to precipitate a solid. The solid was recovered by filtration, washed with anhydrous ethanol and vacuum-dried to give 6.3 g of a yellowish white powder. The yellowish white powder was subjected to elemental analysis and mass analysis and measured for infrared absorption spectrum and NMR spectrum to show that the powder was Compound (7). Fig. 2 shows the infrared absorption spectrum of Compound (7).

Synthesis Example 2

[0046] 5.0 Grams of trimethoxygallium and 100 g of anhydrous ethanol were placed in a flask and stirred. Further, a solution of 9.0 g of 8-hydroxyquinoline in 140 g of anhydrous ethanol was dropwise added, and the mixture was stirred at 60°C for 30 minutes. Further, 5.3 g of 4-hydroxybiphenyl was added, and the mixture was stirred at 70°C for 30 minutes. Then, 4.9 g of 8-hydroxyquinoline was added, and the mixture was stirred at 70°C for 5 hours to precipitate a solid. The solid was recovered by filtration, washed with anhydrous ethanol and vacuum-dried to give 7.2 g of a yellowish white powder. The yellowish white powder was subjected to elemental analysis and mass analysis and measured for infrared absorption spectrum and NMR spectrum to show that the powder was Compound (9). Fig. 3 shows the infrared absorption spectrum of Compound (9).

Synthesis Example 3

[0047] 7.2 Grams of triisopropoxygallium and 100 g of anhydrous ethanol were placed in a flask and stirred. Further, a solution of 9.0 g of 8-hydroxyquinoline in 140 g of anhydrous ethanol was dropwise added, and the mixture was stirred at 60°C for 30 minutes. Further, 5.5 g of 4-cyclohexylphenol was added, and the mixture was stirred at 70°C for 30 minutes. Then, 4.9 g of 8-hydroxyquinoline was added, and the mixture was stirred at 70°C for 5 hours to precipitate a solid. The solid was recovered by filtration, washed with anhydrous ethanol and vacuum-dried to give 7.4 g of a yellowish white powder. The yellowish white powder was subjected to elemental analysis and mass analysis and measured for infrared absorption spectrum and NMR spectrum to show that the powder was Compound (12). Fig. 4 shows the infrared absorption spectrum of Compound (12).

Synthesis Example 4

[0048] 5.0 Grams of trimethoxygallium and 100 g of anhydrous ethanol were placed in a flask and stirred. Further, a solution of 9.0 g of 8-hydroxyquinoline in 140 g of anhydrous ethanol was dropwise added, and the mixture was stirred at 60°C for 30 minutes. Further, 4.5 g of 1-naphthol was added, and the mixture was stirred at 70°C for 30 minutes. Then, 4.9 g of 8-hydroxyquinoline was added, and the mixture was stirred at 70°C for 5 hours to precipitate a solid. The solid was recovered by filtration, washed with anhydrous ethanol and vacuum-dried to give 6.5 g of a yellowish white powder. The yellowish white powder was subjected to elemental analysis and mass analysis and measured for infrared absorption spectrum and NMR spectrum to show that the powder was Compound (16). Fig. 5 shows the infrared absorption spectrum of Compound (16).

Synthesis Example 5

[0049] 5.0 Grams of trimethoxygallium and 100 g of anhydrous ethanol were placed in a flask and stirred. Further, a solution of 9.0 g of 8-hydroxyquinoline in 140 g of anhydrous ethanol was dropwise added, and the mixture was stirred at 60°C for 30 minutes. Further, 4.5 g of 2-naphthol was added, and the mixture was stirred at 70°C for 30 minutes. Then, 4.9 g of 8-hydroxyquinoline was added, and the mixture was stirred at 70°C for 5 hours to precipitate a solid. The solid was recovered by filtration, washed with anhydrous ethanol and vacuum-dried to give 6.6 g of a yellowish white powder. The yellowish white powder was subjected to elemental analysis and mass analysis and measured for infrared absorption spectrum and NMR spectrum to show that the powder was Compound (17). Fig. 6 shows the infrared absorption spectrum of Compound (17).

[0050] The organic EL devices described in the following Examples were measured for light emission brightness with an LS-100 (supplied by Minolta Camera Co., Ltd.). The light emission efficiency η (lm/W) of the devices was determined on the basis of the following equation,

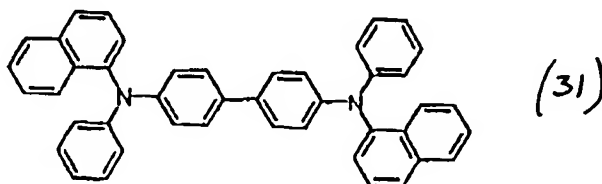
$$\eta(\text{lm/W}) = \pi \cdot L_0 (\text{cd/m}^2) / P_{\text{in}} (\text{W/m}^2)$$

in which P_{in} is an applied power per unit area and L_0 is a brightness obtained by the measurement. In this case, a complete diffusion surface is assumed.

Example 1

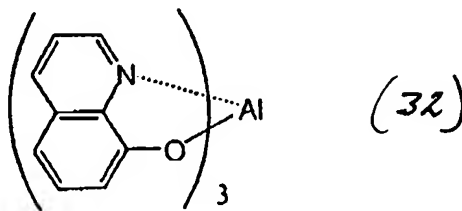
[0051] Compound (31) having the following chemical structure was vacuum-deposited on a cleaned glass substrate with an ITO electrode to form a hole-injecting layer having a thickness of 30 nm. Then, Compound (7) was vapor-deposited thereon to form a light-emitting layer having a thickness of 40 nm. Further, Compound (17) was vacuum-

deposited thereon to form an electron-injecting layer having a thickness of 20 nm. Then, an electrode having a thickness of 150 nm was formed thereon from a magnesium/silver alloy having a magnesium/silver mixing ratio of 10/1, to obtain an organic EL device. The hole-injecting layer, the light-emitting layer, the electron-injecting layer and the cathode were formed by deposition under a vacuum of 10^{-6} Torr at a substrate temperature of room temperature. The organic EL device showed a blue light emission of 16,000 (cd/m^2) at a direct current voltage of 8 V and a light emission efficiency of 2.04 (lm/W).



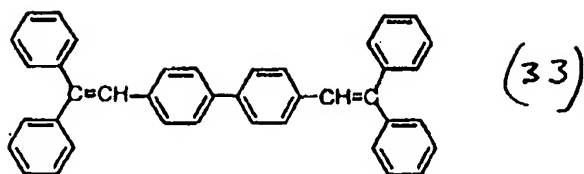
Example 2

[0052] Compound (31) was vacuum-deposited on a cleaned glass substrate with an ITO electrode to form a hole-injecting layer having a thickness of 30 nm. Then, Compound (32) having the following chemical structure was vapor-deposited thereon to form a light-emitting layer having a thickness of 40 nm. Further, Compound (9) was vacuum-deposited thereon to form an electron-injecting layer having a thickness of 20 nm. Then, an electrode having a thickness of 150 nm was formed thereon from an aluminum/lithium alloy having an aluminum/lithium mixing ratio of 100/3, to obtain an organic EL device. The hole-injecting layer, the light-emitting layer, the electron-injecting layer and the cathode were formed by deposition under a vacuum of 10^{-6} Torr at a substrate temperature of room temperature. The organic EL device showed a yellowish green light emission of 13,500 (cd/m^2) at a direct current voltage of 8 V.



Example 3

[0053] Compound (31) was vacuum-deposited on a cleaned glass substrate with an ITO electrode to form a hole-injecting layer having a thickness of 30 nm. Then, Compound (33) having the following chemical structure was vapor-deposited thereon to form a light-emitting layer having a thickness of 40 nm. Further, Compound (9) was vacuum-deposited thereon to form an electron-injecting layer having a thickness of 20 nm. Then, an electrode having a thickness of 150 nm was formed thereon from an aluminum/lithium alloy having an aluminum/lithium mixing ratio of 100/3, to obtain an organic EL device. The hole-injecting layer, the light-emitting layer, the electron-injecting layer and the cathode were formed by deposition under a vacuum of 10^{-6} Torr at a substrate temperature of room temperature. The organic EL device showed a blue light emission of 12,000 (cd/m^2) at a direct current voltage of 8 V.



10 Example 4

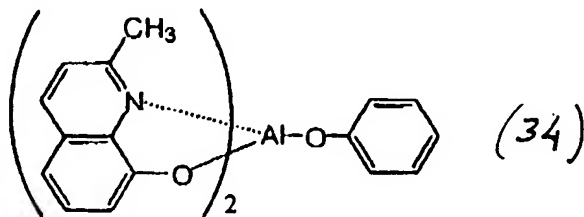
15 [0054] Compound (31) was vacuum-deposited on a cleaned glass substrate with an ITO electrode to form a hole-injecting layer having a thickness of 30 nm. Then, a solution of poly(2,5-hexylthio-p-phenylenevinylene) having a number average molecular weight of 25,000 in chloroform was spin-coated on the hole-injecting layer to form a light-emitting layer having a thickness of 40 nm. Further, Compound (9) was vacuum-deposited thereon to form an electron-injecting layer having a thickness of 20 nm. Then, an electrode having a thickness of 150 nm was formed thereon from a magnesium/silver alloy having a magnesium/silver mixing ratio of 10/1, to obtain an organic EL device. The hole-injecting layer, the electron-injecting layer and the cathode were formed by deposition under a vacuum of 10^{-6} Torr at a substrate temperature of room temperature. The organic EL device showed a greenish yellow light emission of 10,500 (cd/m^2) at a direct current voltage of 8 V.

20 Example 5

25 [0055] Compound (31) was vacuum-deposited on a cleaned glass substrate with an ITO electrode to form a hole-injecting layer having a thickness of 30 nm. Then, Compound (30) was vapor-deposited thereon to form a light-emitting layer having a thickness of 40 nm. Further, Compound (7) was vacuum-deposited thereon to form an electron-injecting layer having a thickness of 20 nm. Then, an electrode having a thickness of 150 nm was formed thereon from an aluminum/lithium alloy having an aluminum/lithium mixing ratio of 100/3, to obtain an organic EL device. The hole-injecting layer, the light-emitting layer, the electron-injecting layer and the cathode were formed by deposition under a vacuum of 10^{-6} Torr at a substrate temperature of room temperature. The organic EL device showed a bluish green light emission of 15,000 (cd/m^2) at a direct current voltage of 8 V and a light emission efficiency of 2.35 (lm/W).

30 Comparative Example 1

35 [0056] An organic EL device was obtained in the same manner as in Example 1 except that Compound (7) for a light-emitting material was replaced with Compound (34) having the following chemical structure. The organic EL device was measured for a light emission brightness. The organic EL device showed a yellowish green light emission of 11,000 (cd/m^2) at a direct current voltage of 8 V and a light emission efficiency of 0.81 (lm/W). It was found that the light emission was made from Compound (34).



Comparative Examples 2 - 3

55 [0057] Organic EL devices were obtained in the same manner as in Example 5 except that Compound (7) for an electron-injecting layer was replaced with compounds shown in Table 3. The organic EL devices were measured for light emission brightness at a direct current voltage of 8 V.

Table 3

	Electron-injecting material	Brightness (cd/m ²)	Light emission efficiency (lm/W)
Example 5	Compound (7)	15,000	2.35
Comparative Example 2	Compound (32)	9,500	1.15
Comparative Example 3	Compound (34)	6,500	0.80

[0058] The organic EL devices obtained in the above Examples, having the structure of at least 2 layers, showed a light emission color of from blue to bluish green, a light emission brightness of at least 5,000 cd/m² and high light emission efficiency. Further, when the organic EL devices obtained in the above Examples were allowed to continuously emit light at 3 mA/cm², all the organic EL devices emitted light having a brightness of at least 1/2 of the initial brightness for more than 10,000 hours. The organic EL device obtained in Example 5 had a stable light emission brightness for more than 10,000 hours and showed almost no dark spots, while the organic EL devices obtained under the same conditions in Comparative Examples 2 and 3 showed light emission brightnesses which decreased to 1/2 or less of the initial brightness within 500 hours. Further, the organic EL devices obtained in Comparative Examples 2 and 3 showed many dark spots, and with the passage of time in measurement, the number of dark spots increased, and the sizes thereof increased. The reason therefor is assumed to be as follows. Compounds used in place of the compound of the present invention was poor in adhesion to the light-emitting layer and to the cathode and in formability, and the light-emitting layer and the cathode were greatly different in work function. The above results show that the use of the gallium complex of the present invention in a layer between the light-emitting layer and the cathode gives an organic EL device having a high light emission efficiency and an increased device life.

[0059] The organic EL device according to the present invention accomplishes improvements in light emission efficiency and brightness, and achieves an increased device life. There is therefore no limitation to be imposed on the light-emitting material, dopant, hole-injecting material, electron-injecting material, sensitizer, resin and electrode material which are used in combination of the gallium complex of the present invention, nor is the method of producing the device limited.

[0060] An organic EL device having a layer formed of the gallium complex of the present invention between a light-emitting layer and a cathode exhibits a high light emission efficiency and an increased device life as compared with conventional organic EL devices. When the gallium complex of the present invention is used to form at least one layer of an organic EL device, the organic EL device exhibits a high light emission brightness, a high light emission efficiency and a long device life.

[0061] As used herein, an alkyl group or moiety is typically a C₁-C₁₈ alkyl group or moiety, preferably a C₁-C₈ alkyl group or moiety, more preferably a C₁-C₆ alkyl group or moiety. Substituted alkyl groups include haloalkyl groups, for example chloro- or fluoro-alkyl groups which may comprise one or more halogen substituents.

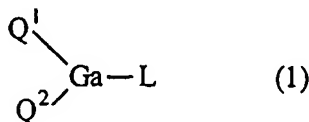
[0062] An aryl group or moiety is typically a C₅-C₁₆ aryl group or moiety, preferably a C₅-C₁₄ aryl group or moiety, more preferably a C₅-C₁₀ aryl group or moiety. An aryl group or moiety may be substituted by one or more substituents such as a halogen, alkyl, alkoxy or nitro substituent. A mono or di substituted amino group is typically substituted by one or two alkyl, aryl or acyl moieties.

[0063] An acyl group or moiety is typically a C₂-C₆, preferably a C₂-C₄ acyl group or moiety. A carbamoyl group is typically substituted by one or two alkyl or aryl moieties. A cycloalkyl group or moiety is typically a C₃-C₆ cycloalkyl group or moiety. A heterocyclic group is typically a 3 to 14 membered heterocyclic group, preferably a 4 to 10 membered heterocyclic group containing one, two or three heteroatoms selected from N, O and S.

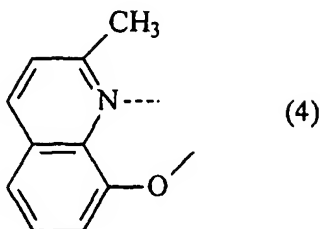
[0064] Specific examples of R¹, as defined above, include those described concerning the rings A¹ and A².

Claims

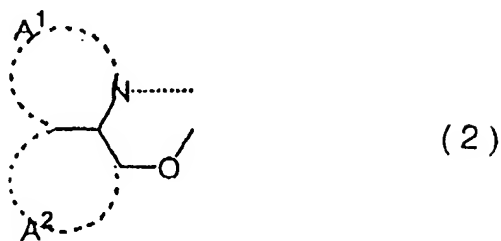
1. Use of a compound of formula (1) in an electron injecting layer of an organic electroluminescence device,



wherein at least one of Q¹ and Q² is a ligand of formula (4),



the other being a ligand of the general formula (2),



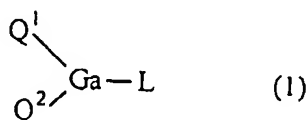
wherein A¹ and A² are substituted or unsubstituted six-membered aryl rings which are mutually fused to form a fused ring moiety, and

L is -OR¹ in which R¹ is a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group or a substituted or unsubstituted aryl group.

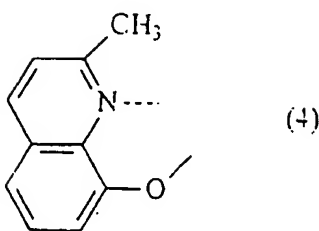
- 30
2. Use according to claim 1, wherein Q¹ and Q² are both ligands of the formula (4).
 3. An organic electroluminescence device comprising a plurality of thin organic compound layers including a light-emitting layer and an electron-injecting layer, sandwiched between an anode and a cathode, wherein the electron-injecting layer comprises a compound of formula (1), as defined in claim 1 or 2.
 4. A device according to claim 3 wherein at least one of the layers comprises an arylamine derivative.
 5. A wall-mountable TV set, a light source for a copying machine or a printer, a light source for a liquid crystal display or a counter, a display board or a sign lamp containing, as a flat light-emitter, an organic electroluminescence device as claimed in claim 3 or 4.
- 40

45 Patentansprüche

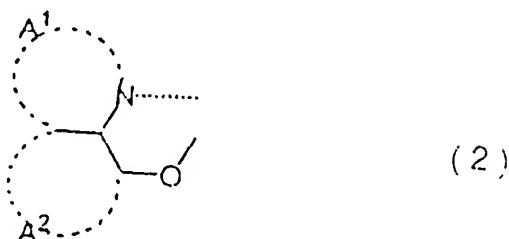
1. Anwendung einer Verbindung der Formel (1) in einer Elektronen-injizierenden Schicht einer organischen Elektrolumineszenz-Vorrichtung,



wobei mindestens eines von Q¹ und Q² ein Ligand der Formel (4) ist,



wobei das andere ein Ligand der allgemeinen Formel (2) ist,



25 worin A¹ und A² substituierte oder unsubstituierte sechsgliedrige Arylringe sind, die zur Bildung einer verschmolzenen Ringkomponente miteinander verschmolzen sind, und
L -OR¹ ist, worin R¹ ein Wasserstoffatom, eine substituierte oder unsubstituierte Alkylgruppe, eine substituierte oder unsubstituierte Cycloalkylgruppe oder eine substituierte oder unsubstituierte Arylgruppe ist.

30

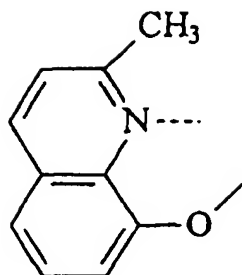
2. Anwendung nach Anspruch 1, worin sowohl Q¹ als auch Q² Liganden der Formel (4) sind.
3. Organische Elektrolumineszenz-Vorrichtung, umfassend eine Vielzahl von Dünnschichten einer organischen Verbindung, einschließlich einer lichtemittierenden Schicht und einer Elektronen-injizierenden Schicht, eingebracht zwischen eine Anode und eine Kathode, wobei die Elektroneninjizierende Schicht eine Verbindung der Formel (1) umfaßt, wie in Anspruch 1 oder 2 definiert.
- 35
4. Vorrichtung nach Anspruch 3, wobei mindestens eine der Schichten ein Arylamin-Derivat umfaßt.
- 40
5. Wandhängbares TV-Gerät, Lichtquelle für ein Kopiergerät oder einen Drucker, Lichtquelle für eine Flüssigkristallanzeige oder ein Zählwerk, Anzeigetafel oder Signallampe, enthaltend, als eine flache lichtemittierende Einrichtung, eine organische Elektrolumineszenz-Vorrichtung, wie in Anspruch 3 oder 4 beansprucht.

45 Revendications

1. Utilisation d'un composé ayant la formule (1) dans une couche d'injection d'électrons d'un dispositif à électroluminescence organique,

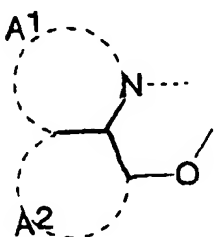


dans lequel au moins un élément parmi Q¹ et Q² est un ligand ayant la formule (4),



(4)

l'autre étant un ligand ayant la formule générale (2),



(2)

où A¹ et A² sont des noyaux aryle à six éléments substitués ou non substitués qui sont mutuellement fusionnés pour former une fraction à noyaux fusionnés, et

L est -OR¹, où R¹ est un atome d'hydrogène, un groupe alkyle substitué ou non substitué, un groupe cycloalkyle substitué ou non substitué ou un groupe aryle substitué ou non substitué.

2. Utilisation selon la revendication 1, dans laquelle Q¹ et Q² sont tous deux des ligands ayant la formule (4).
3. Dispositif à électroluminescence organique comportant une pluralité de couches minces de composés organiques incluant une couche émettrice de lumière et une couche d'injection d'électrons, enserrées entre une anode et une cathode, la couche d'injection d'électrons comportant un composé ayant la formule (1), telle que définie dans la revendication 1 ou 2.
4. Dispositif selon la revendication 3, dans lequel au moins une des couches comporte un dérivé d'arylamine.
5. Poste de télévision pouvant être monté sur un mur, source de lumière pour une machine de reproduction ou une imprimante, source de lumière pour un affichage à cristaux liquides ou un compteur, tableau d'affichage ou lampe signalétique contenant, en tant qu'émetteur de lumière plat, un dispositif à électroluminescence organique selon la revendication 3 ou 4.

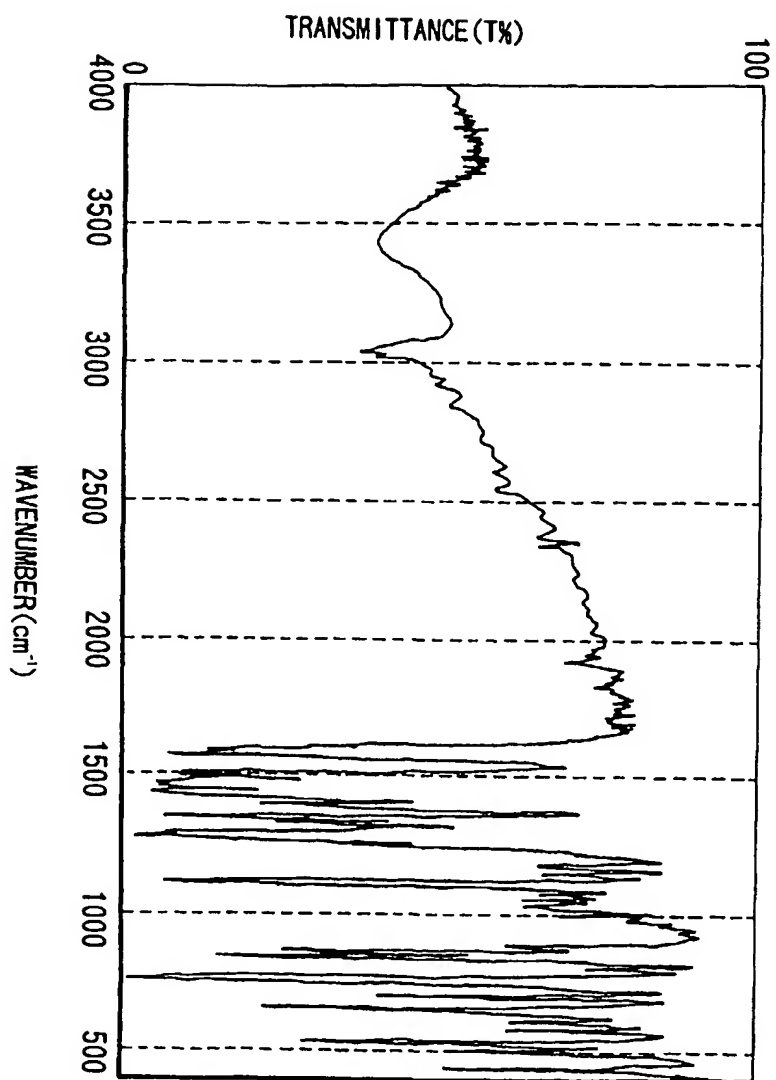


FIG.2

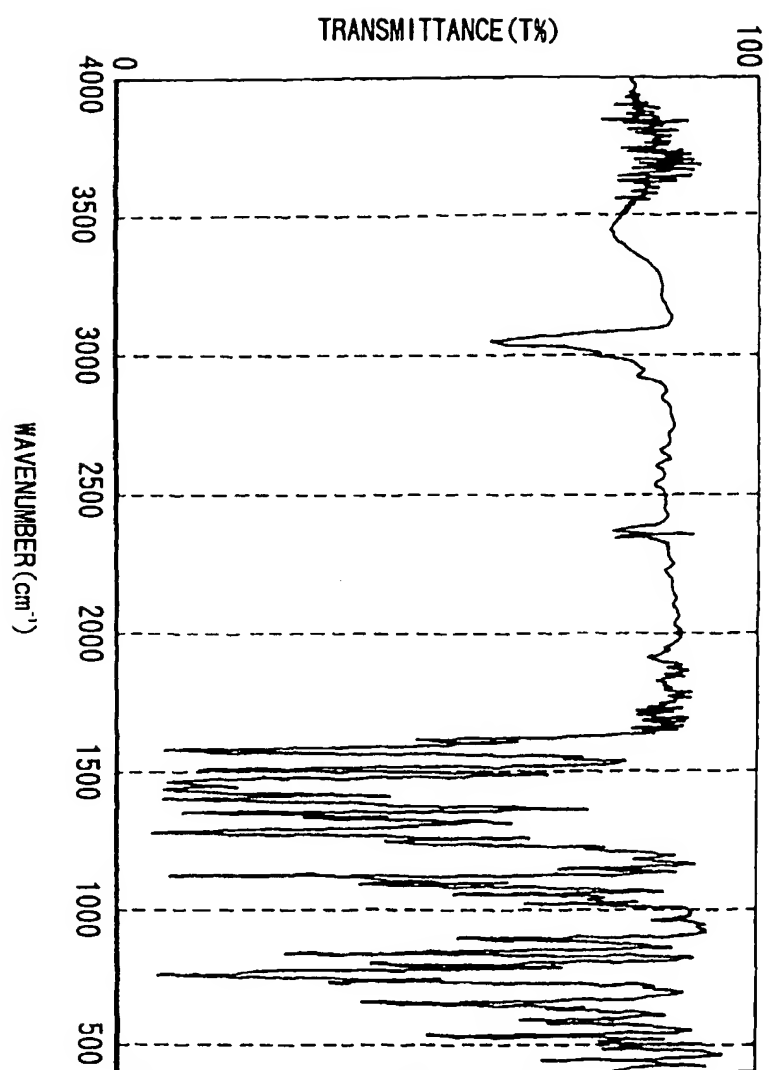


FIG.3

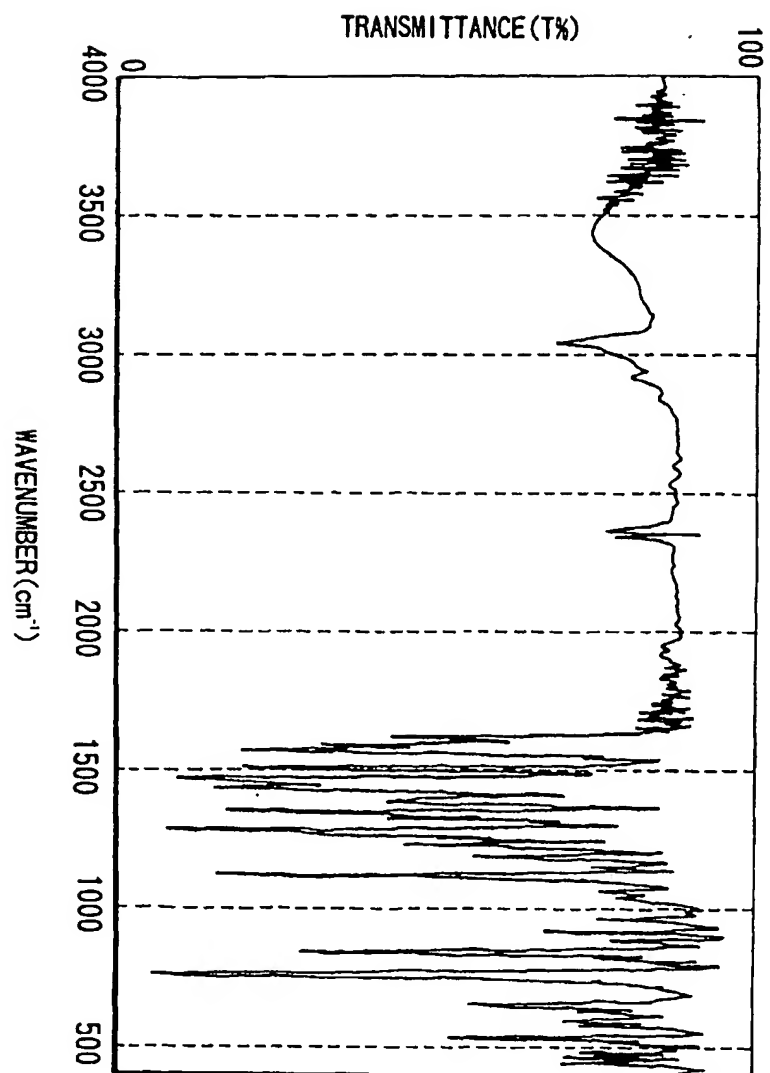


FIG.4

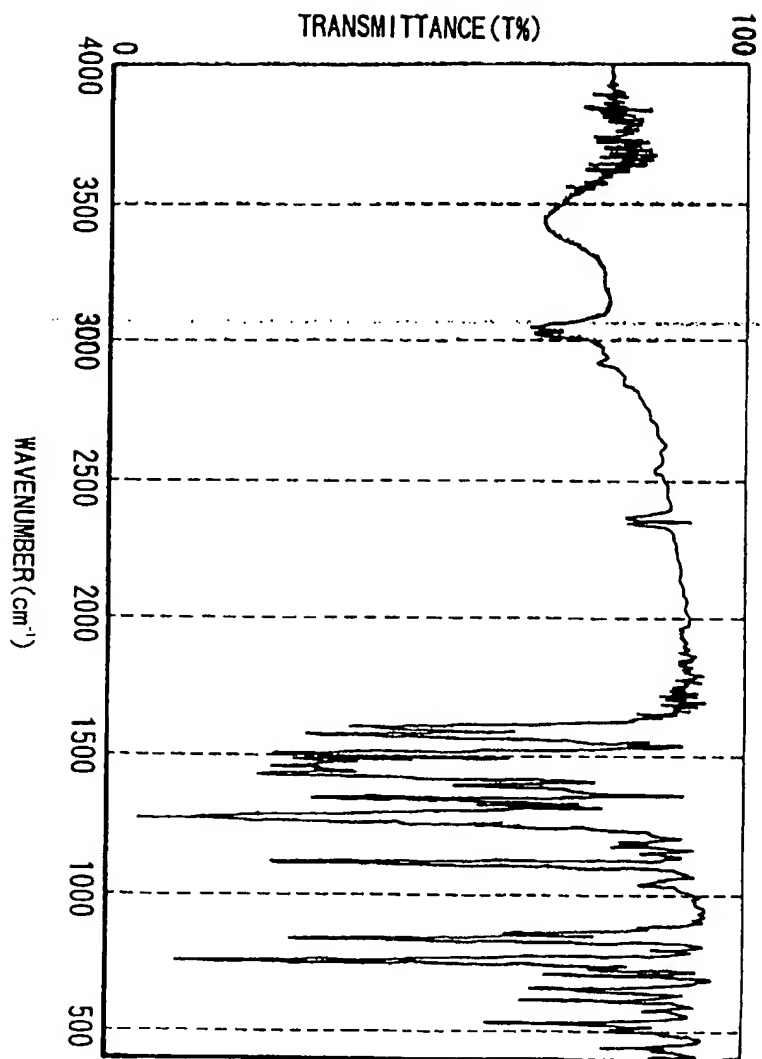


FIG.5

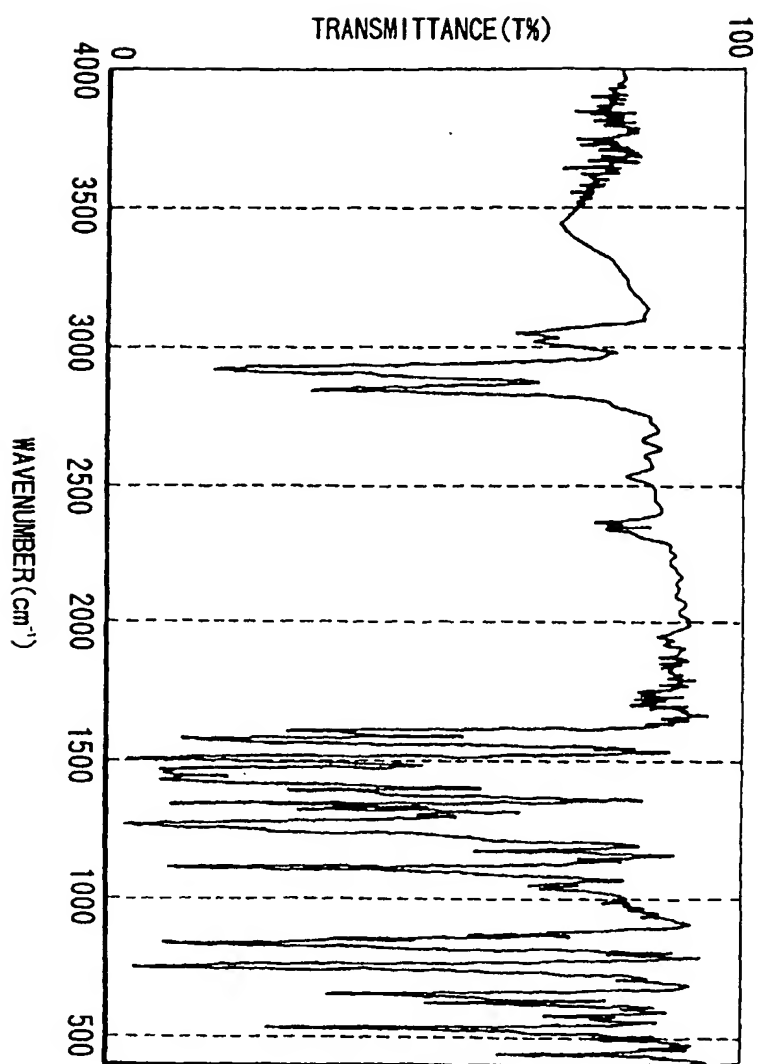


FIG.6